

PATENT SPECIFICATION

818.069



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COMPLETE SPECIFICATION

Improvements to Infra-Red Sensitive Luminescent Materials

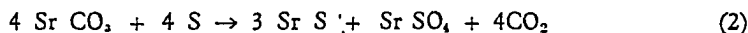
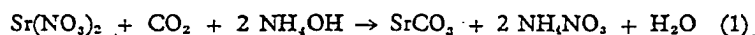
We, SOCIÉTÉ NOUVELLE DE L'OUTILLAGE R.B.V. ET DE LA RADIO-INDUSTRIE—43—45 Avenue Kleber, Paris 16^{ème}, France, a French Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the preparation of infra-red sensitive luminescent materials which will be called hereafter "phosphors".

Infra-red sensitive phosphors are well known in the prior art. One particular type of such phosphors gives a visible picture under stimulation by infra-red radiations provided it has been previously excited by a radiation of shorter wave length than the visible light which is emitted (usually, the phosphor is excited by ultra-violet radiations). Such a type of phosphors has been described in British Patents No. 650,455—650,458—650,459 and the terminology used here is fully explained in these patents.

A particularly interesting phosphor of this type has been described in Peter Brauer's publication "Über eine Gruppe von Mischphosphoren mit gemischten Aktivatoren" Zeitschrift für Naturforschung, February 1946, pages 70—78, in which the author describes a phosphor comprising a matrix of strontium sulphide activated by cerium and samarium, U.S. Patent No. 2,485,903 (Neville F. Miller) concerns the addition of lead to the two previously cited activators. The type of infra-red phosphor comprising strontium sulphide, the three activators and auxiliary flux material will be called "phosphor of the type described".

A known process of manufacture of the phosphors of the type described is to purify a strontium nitrate solution to the highest degree obtainable. The nitrate is transformed into carbonate which is decomposed in the presence of sulphur so as to produce a mixture of strontium sulphide and sulphate. The reactions which are used are shown in the following equations:



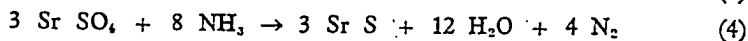
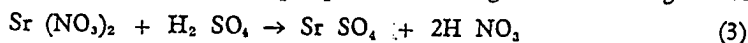
The strontium sulphide obtained contains a high percentage of strontium sulphate. Though it has been stated in British Patent 650,458 that the presence of sulphate did not matter, it is necessary to eliminate the sulphate, in order to obtain a highly stimuable phosphor. According to prior art, the sulphate is reduced by hydrogen sulphide. According to the inventors' experience, the phosphors obtained through this process show a poor stimulability. This poor sensitivity may be due both to the presence of inactive strontium sulphate in the sulphide and to traces of heavy metal salts in the strontium sulphide matrix. Actually traces of heavy metals of the order of 10^{-7} concentration produce a decrease in the stimulability of the powder.

[Price 3s. 6d.]

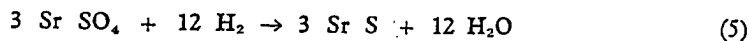
The present invention provides a process of manufacturing a phosphor of the type described, which process comprises using a matrix of strontium sulphide obtained from highly purified strontium nitrate by reaction with sulphuric acid and further reduction with ammonia or hydrogen at 1,000° C., and using a lithium fluoride flux obtained from lithium sulphate. In the process of the invention it is preferred to purify the strontium sulphide matrix, *inter alia*, by means of at least two organic reagents used successively at predetermined pH and temperature conditions. One way of effecting purification of the strontium nitrate is (i) by means of at least two organic reagents used successively namely oxyquinoline and diphenylthiocarbazone which give

compounds insoluble in the nitrate, (ii) a fractional crystallization and (iii) a second chemical purification. Another way of effecting purification of the strontium nitrate is by means successively of oxyquinoline at two different pH values and of diphenylthiocarbazone at three different pH values.

Suitably, in the process of the invention, the purification of the basic chemicals which are used in the manufacture of the phosphors



with ammonia or



with hydrogen.

According to a particular method of effecting the process of the invention, the basic chemicals which are used in the manufacture of the phosphors of the type described (namely the strontium nitrate to manufacture strontium sulphide matrix and the lithium sulphate used to obtain the lithium fluoride used as a flux) are purified by reactions with diphenylthiocarbazone (or dithizone) and oxyquinoline (i.e. oxine), the heavy metal insoluble compounds formed being eliminated from the solution by means of specific solvents such as chloroform and carbon tetrachloride, said first chemical purification being followed by a fractional crystallization and a second chemical purification.

According to a preferred method of effecting the method of the invention, purification of the basic chemicals is obtained by a chemical purification by organic reagents with a control of the temperature and the operating pH of each reaction. It is well known to use organic reagents in colorimetric chemical analysis to find out whether there are traces of heavy metals in a solution of metallic salt. Said reagents give compounds which are insoluble in the solution but are soluble in organic solvent. Such an analysing processing is described for instance in "Colorimetric determination of traces of metals" by E. B. Sandell, published by Interscience Publishers Inc. The use of particular reagents at controlled pH and temperature conditions is made according to the invention to eliminate traces of heavy metals from the basic chemicals used in the preparation of the phosphors of the type described. The complete elimination of the traces of heavy metal is easily controlled owing to the fact that the insoluble compounds which are obtained by reaction between the heavy metals and the organic reagents produce a coloration of the specific solvent. As will be described, the inventors have found that the use of dithizone and oxine respectively at two and three successive values of pH, at room temperature, gives a complete elimination of stimulation reducing

is obtained by using two or several organic reagents which give compounds with the heavy metals which are insoluble and removable by means of selective solvents.

Suitably also, in the process of the invention, the matrix of strontium sulphide is obtained in acid medium by reaction of sulphuric acid on strontium nitrate and reduction of the sulphate by hydrogen or ammonia according to the following reactions:

heavy metal traces.

In carrying out the process of the invention it is suitable to take special care to wash and purify the vessels and auxiliary chemicals which are used in the preparation of said phosphors.

The preparation of a phosphor according to the process of the invention will be described in detail and the characteristics of the phosphor powder obtained are shown on Figures 3 and 4 of the accompanying diagrammatic drawings. Figures 1 and 2 of said drawings show the block diagrams of the different operations necessary to prepare the phosphor according to the invention. Figure 2 shows a preferred embodiment of the invention in which the purification of the basic chemicals involved is obtained only through chemical purifications. The other operations are the same in both embodiments of the invention.

I—WASHING OF VESSELS—

This operation is not shown on the block diagram though special care must be taken in view of obtaining the high sensitivity phosphor. The glass vessels are first washed in a hot solution of caustic soda at 5%. They are rinsed in boiling nitric acid or in vapors of nitric acid and then rinsed with water which has been distilled three times. The vessels in sintered alumina which are necessary to some operations are washed in boiling nitric acid and rinsed in water which has been distilled three times.

II—PURIFICATION OF AUXILIARY CHEMICALS—

Water is distilled a first time in an ordinary glass still, a second time in a still in "Pyrex" (Registered Trade Mark) glass, and a third time in a silica still.

Ethyl alcohol is distilled twice successively in "Pyrex" glass stills.

Chloroform and carbon tetrachloride are distilled twice in "Pyrex" glass stills.

Nitric acid is distilled twice in "Pyrex" glass stills.

Sulphuric acid is distilled twice in "Pyrex" glass stills under reduced pressure.

Sulphur is distilled six times successively in a "Pyrex" glass apparatus under reduced pressure and then crystallized in carbon sulphide.

5 Hydrofluoric acid is distilled twice in platinum stills or stills of an organic material which is not attacked by hydrofluoric acid (Teflon).

10 Carbon sulphide is distilled twice in a "Pyrex" glass apparatus.

III—PURIFICATION OF THE BASIC CHEMICALS—

As was said, the matrix of the phosphor (strontium sulphide) is obtained from strontium nitrate. An aqueous solution of nitrate with a concentration between 10 and 50% is mixed up with a solution of oxyquinoline in chloroform or carbon tetrachloride the concentration of which is comprised between 0.001% and 1%, taking approximately 98% of the nitrate solution and 2% of the oxyquinoline solution. After stirring, the solution is left to rest. The initial solution of oxyquinoline in chloroform is pale yellow. The oxyquinoline constitutes compounds with some heavy metals which modify the coloration of the oxyquinoline solution and which are not miscible in the aqueous nitrate solution. The coloured oxyquinoline solution is removed and a new quantity of fresh yellow solution of oxyquinoline is added to the strontium nitrate. The mixture is stirred up and so on. This operation is repeated until the oxyquinoline solution remains its initial colour (pale yellow) after stirring. The strontium nitrate solution is then purified by means of a second reagent called dithizone. This reagent is used as a green solution in chloroform or carbon tetrachloride (concentration between 0.001% and 1%). The processing is the same as with the oxyquinoline solution. After these two purifications, the solution of strontium nitrate is crystallized six times; for each crystallization 1/6 of the solution is wasted. It is then proceeded to a new purification with both reagents (oxyquinoline and dithizone).

Another basic chemical is lithium sulphate which is the initial material for the lithium fluoride used as a flux. An aqueous solution of lithium sulphate with a concentration between 6 and 30% is chemically purified in the same way as the strontium nitrate solution, that is by addition of a solution of oxyquinoline and of a solution of dithizone. The solution undergoes then six fractional crystallizations. At each stage 1/6 of the solution is wasted. The solution is then processed once more with both oxyquinoline and dithizone.

60 IV—STRONTIUM SULPHIDE PREPARATION—

An excess of twice distilled sulphuric acid is added to the solution of strontium nitrate. Strontium sulphate forms a precipitate which is washed several times with the distilled water and twice with the distilled ethyl alco-

hol. It is then dried under vacuum. The strontium sulphate is then reduced to sulphide by ammonia at 1,000° C. or by hydrogen according to the reactions which have been written above. This reduction takes place in a rotating crucible of sintered alumina. The sulphate is introduced in the crucible and a current of ammonia or hydrogen is passed through in the apparatus. In the crucible the operation is controlled by condensing the water vapor which is formed in a cooled vessel. When the condensation stops, the heating is continued at the same temperature for half an hour.

V—LITHIUM FLUORIDE PREPARATION—

A current of ammonia is passed through the distilled hydrofluoric acid until neutralization. The correct molecular quantity of the ammonium fluoride thus obtained is added to the correct molecular quantity of lithium sulphate. The precipitate of lithium fluoride is poured off and washed once in distilled water and once in distilled alcohol. It is then dried under vacuum.

VI—ACTIVATORS PREPARATION—

The solution of cerium, samarium and lead are obtained by dissolving one part of nitrate of each of said metals in 99 parts of methyl alcohol.

VII—PROCESSING OF THE PHOSPHOR—

95 parts of strontium sulphide are mixed and stirred with 5 parts of lithium fluoride. Twice distilled hexane is added so as to obtain a thick paste. Then the activators are added with the following concentrations:

cerium 100 to 150 mg/kg of phosphor
samarium 20 to 30 mg/kg of phosphor, and
lead 30 to 40 mg/kg of phosphor

It will be seen that the quantity of cerium nitrate solution added to one kilogram of the mixture of strontium sulphide and lithium fluoride is 145 milligrams in one particular phosphor.

The mixture is heated in a sintered alumina crucible at 1,000° C. during 20 minutes in a current of purified nitrogen. Once cooled at room temperature, the mixture is milled and screened through a mesh corresponding to the required size of the powder (generally between 30 and 50 μ). The powder is baked with 3 to 10 decigrams of sulphur per kg. of powder in a sintered alumina crucible having a capacity of about 1 litre for 20 minutes at 640 degrees in a current of purified nitrogen. When the powder has been screened a second time, it is ready for use.

The reason for heating the powder with the sulphur is to diminish the decrease of sensitivity following the milling. After milling and sifting the powder contains a lot of air, its apparent density being about 1 to 1.3 kg./litre whereas the density of melted strontium sulphide is 3.7 kg./litre. Thus, one litre of powder contains:

1—1/3.7 = 0.73 litre of air which includes

0.152 litres of oxygen.

When the powder with sulphur is heated to 250° C., this oxygen is removed in the form of SO₂ and SO₃, and the oxidization of the powder is avoided. In addition, if the powder is partially transformed into hydroxide during the milling and sifting as a result of humidity, this hydroxide is transformed by the SO₂ and SO₃ in gas form into sulphate which is less harmful to the powder. Above 445° C. the excess sulphur is vaporized and is driven off together with the SO₂ and SO₃ gases which are not fixed as well as the water vapor formed by the decomposition of the hydroxide.

It should be noted that strontium sulphide is attacked by water vapor and changed to hydroxide. Therefore from the reduction of the sulphate on, all the operations should be undertaken in moisture-proof apparatus. For the same reason, the powder should be stocked in water-tight flasks or flasks with a desiccator.

VIII—PREFERRED PURIFICATION OF THE BASIC CHEMICALS—

Figure 2 shows the block diagram of the preferred processing of chemical purification of both strontium nitrate and lithium sulphate.

The operation is slightly different from the chemical purification previously described and the following steps should be carefully followed. The reagents used are successively oxyquinoline and diphenylthiocarbazone. The aqueous solution of strontium nitrate (a concentration of 350 grams of anhydrous nitrate per litre of water) is poured in a flask 1 (Figure 5) containing approximately 20 litres. A stirrer 2 is dipping in the liquid. The solution is brought to pH = 4 for the first operation by addition of ammonia or acetic acid according to the pH of the initial solution. The solution of oxyquinoline in chloroform at 1% is introduced through burette 3. The quantity is 150 cm³ for 20 to 15 litres of nitrate solution. The mixture is stirred for several minutes so that the organic solution of reagent constitutes an emulsion with the aqueous solution so as to provide an intimate contact between the reagent and the nitrate. The stirrer is stopped and the solution is left still for a few minutes until the nitrate and the organic solution are separated. The organic solution which is heavier falls to the bottom of

the flask and fills up appendix 4 which is intended for this purpose. The appendix makes it easier to see the colour of the organic solution which fills it by gravity. The organic solution which is pale yellow, shows different colorations successively black, dark green and yellowish green when added to the nitrate. The organic solution is then poured off from the flask by means of pipe 5 of a siphon. Pipe 5 is introduced in the flasks until its end goes into appendix 4. The siphon is initiated by depression at the end of pipe 6 by means of a water pump connected at 7. It is easy to stop the siphon when appendix 4 is filled with the nitrate solution. The same quantity of fresh organic solution is then added. This operation is repeated until the reagent keeps its initial colour (pale yellow). The nitrate solution is then washed several times with the specific solvent of the reagent (chloroform) until the whole reagent has been eliminated. The washing is stopped when the chloroform remains colourless (the oxyquinoline gives a yellow coloration to the chloroform). A second series of operations is performed at pH = 7 with the same reagent at room temperature. Then the same processing takes place with a solution of dithizone in carbon tetrachloride with a concentration between 10⁻⁴ and 10⁻⁵. The initial solution is green; the pure carbon tetrachloride is colourless. A first series of operations takes place at pH = 4. The organic compounds obtained are successively blue—green. A second operation is performed at pH = 7 and a third one at pH = 10. At pH = 10 the dithizone becomes soluble in water and the whole nitrate solution becomes orange. The heavy metal impurities which give compounds with the dithizone give a reddish coloration to the organic solution. The purification at pH = 10 is repeated until the organic solution in appendix 4 remains green. The whole solution is then washed with pure carbon tetrachloride until the tetrachloride remains colourless. The following table will give (by their chemical symbols) the list of the different metals which are eliminated by each of the operations which have been described. The figure which follows the symbol corresponds to the valence of the metal.

Reagent	pH 4 Metals	pH 7 Metals	pH 10 Metals
Oxyquinoline or oxine 1% in chloroform	Mo VI Sn IV Fe III Cu II Sb	Fe III Cu II Ni II Bi III Cd Co II Mn Th Ti Zn II	
Diphenylthiocarbazon or dithizone 0,1% to 0,01% in carbon tetra- chloride	Ag I Sn II Hg I and II Cu II Bi III Au Pt	Ag I Bi III Co II Cu II Fe II Hg II Sn II Zn II	Hg I and II Pb II Tl Zn II In

Figures 3 and 4 show the characteristics of the phosphor obtained according to the invention. Curve 1 of Figure 3 shows the luminance L_{IR} in international micro-candels per cm² or micro stilb of a phosphor layer stimulated by an infra-red radiation of 2 microwatt/cm², with respect to the time measured in hours after the excitation.

Curve 2 shows the spontaneous phosphorescence L_{PS} in 10⁻¹ microstilb and curve 3 shows the ratio $\frac{L_{IR}}{L_{PS}}$ which is a measurement

of the contrast. It may be seen that the best contrast (213) is obtained six hours after excitation. The excited phosphorescence corresponds at this moment to the emission of the phosphor layer which would be obtained through stimulation by an infra-red energy of 2/213 microwatt/cm², that is approximately 10⁻⁸ watt/cm². Curve 4 of figure 4 shows the degree of sensitivity of stimulation with respect to time, in days from the time of the excitation. The sensitivity falls to 50% of its initial value four days after excitation and to 18% one month later.

WHAT WE CLAIM IS:—

1. A process of manufacturing a phosphor of the type described, which process comprises using a matrix of strontium sulphide obtained from highly purified strontium nitrate by reaction with sulphuric acid and further reduction with ammonia or hydrogen at 1,000° C., and using a lithium fluoride flux obtained from lithium sulphate.

2. A process according to claim 1, in which the strontium sulphide matrix is purified by means of a least two organic reagents used successively at predetermined pH and temperature conditions.

3. A process according to either one of the two preceding claims, in which the strontium nitrate is purified (i) by means of at least two organic reagents used successively namely oxyquinoline and diphenylthiocarbazon which give compounds insoluble in the nitrate, (ii) a fractional crystallization and (iii) a second chemical purification.

4. A process according to either of claims 2 and 3, in which the strontium nitrate is purified by means successively of oxyquinoline at two different pH values and of diphenylthiocarbazon at three different pH values.

5. A process according to any one of the preceding claims, in which there is used per kg. of phosphor the following activators in the concentrations mentioned:—

cerium 100 to 150 mg.,
samarium 20 to 30 mg., and
lead 30 to 40 mg.

6. A process according to claim 1 substantially as herein described with reference to Figure 1 or Figure 2 of the accompanying diagrammatic drawings.

7. A phosphor of the type described whenever produced by the process claimed in any one of the preceding claims.

MEWBURN ELLIS & CO.,

70 & 72, Chancery Lane, London, W.C.2,
Chartered Patent Agents.

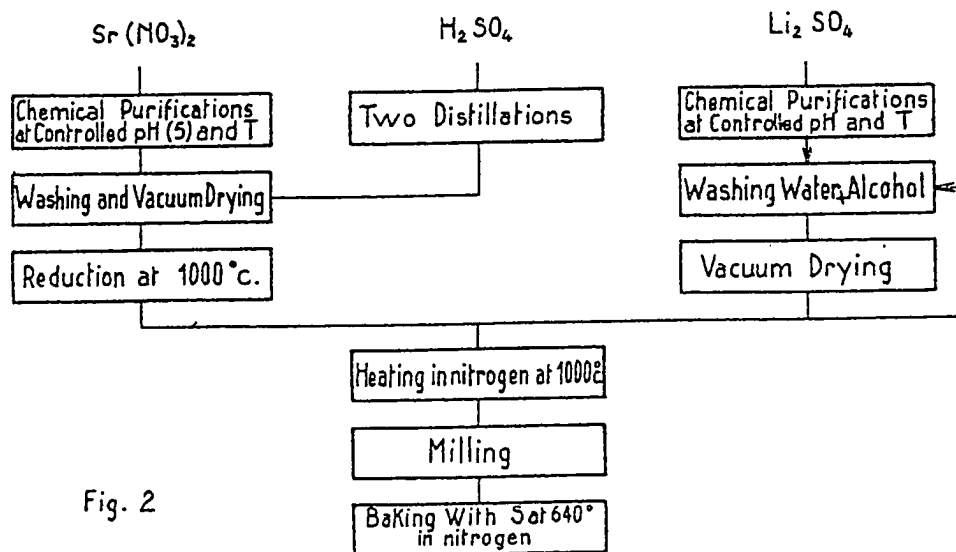
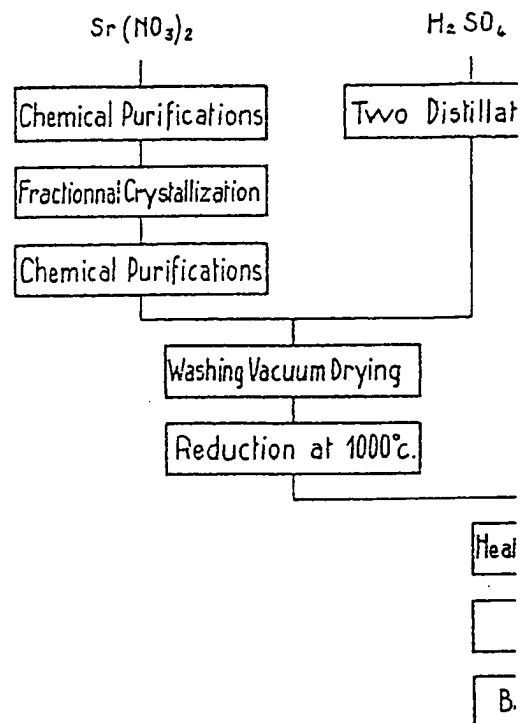


Fig. 2

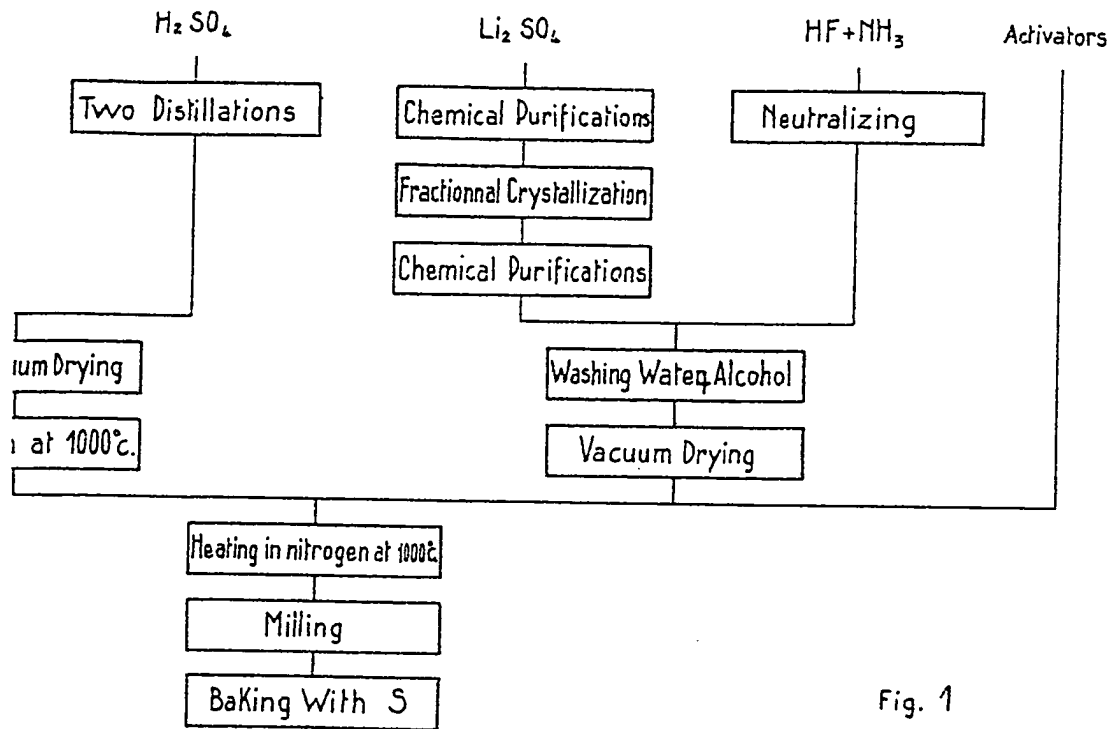
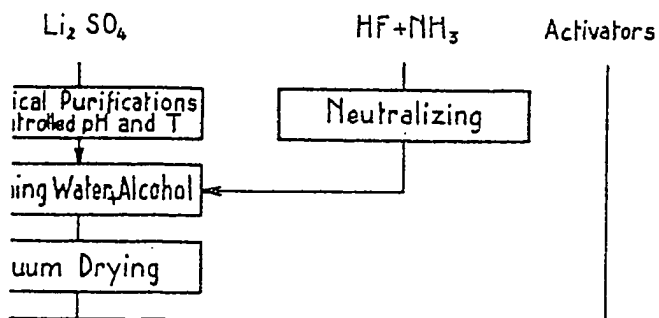


Fig. 1



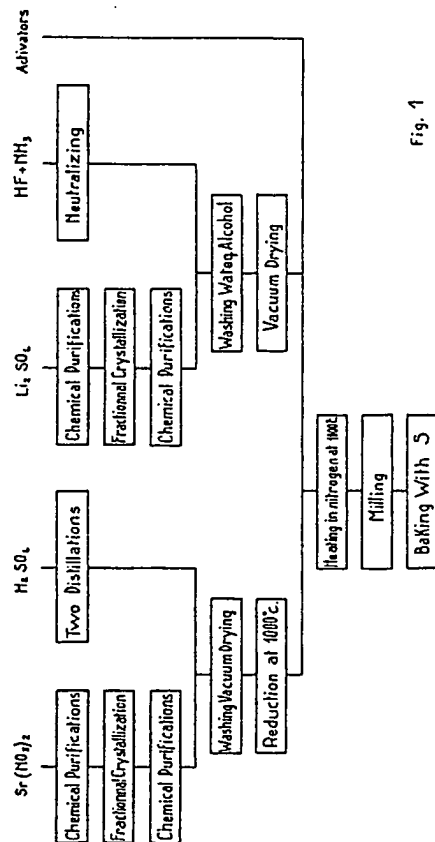


Fig. 1

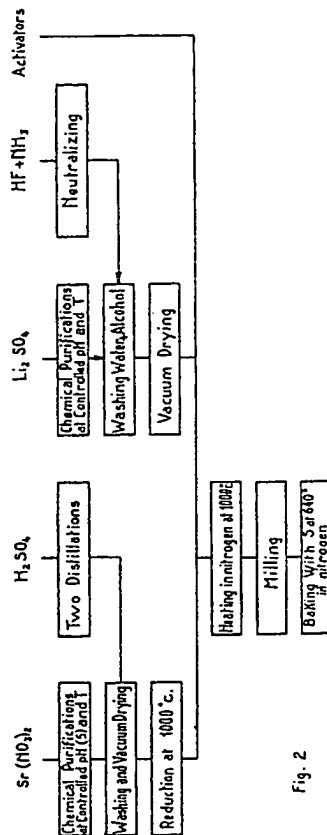


Fig. 2

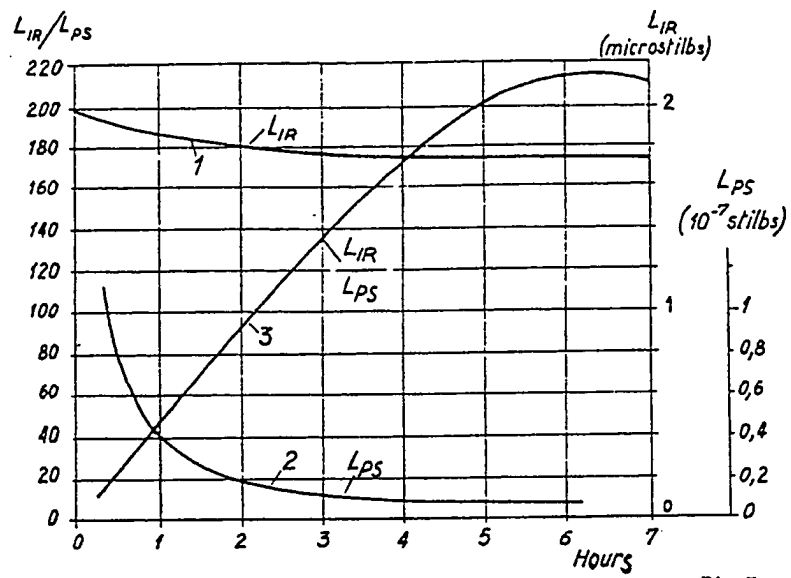


Fig.3

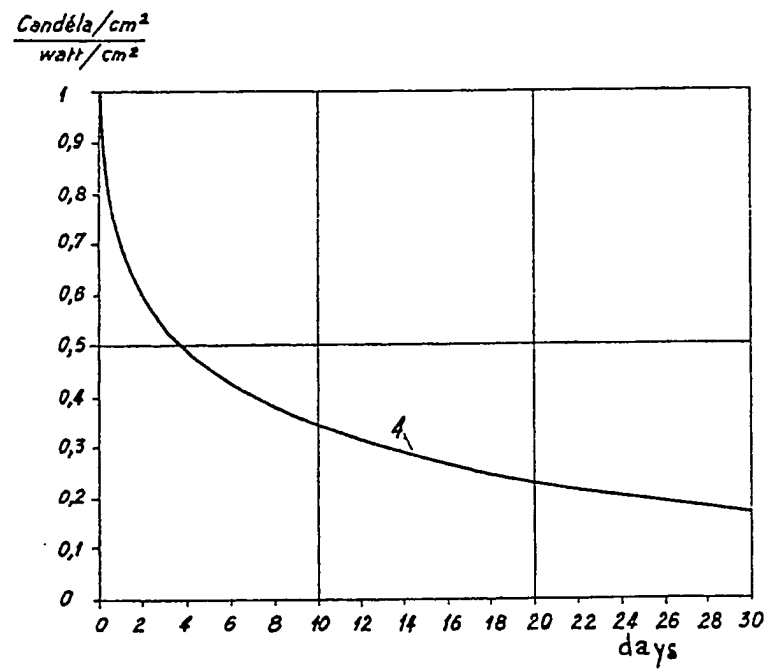


Fig.4

818,069 COMPLETE SPECIFICATION

3 SHEETS

*This drawing is a reproduction of
the Original on a reduced scale.*

SHEETS 2 & 3

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kilbs)

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0,8
0,6
0,4
0,2
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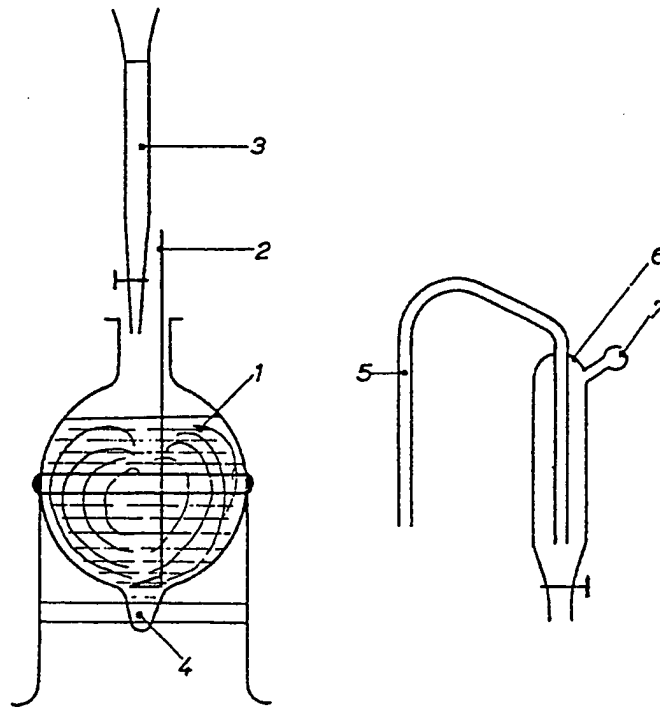


Fig 5

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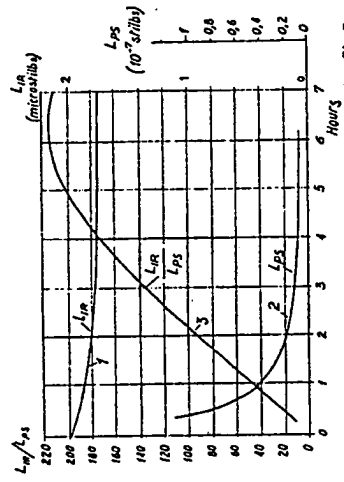


Fig. 3

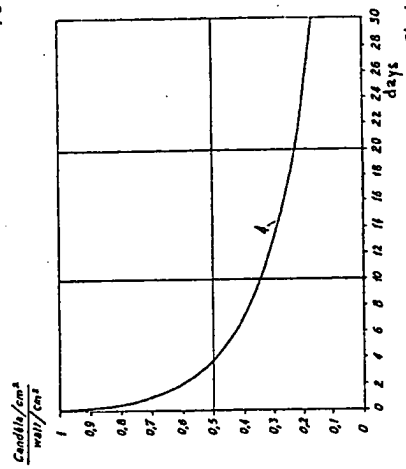


Fig. 4

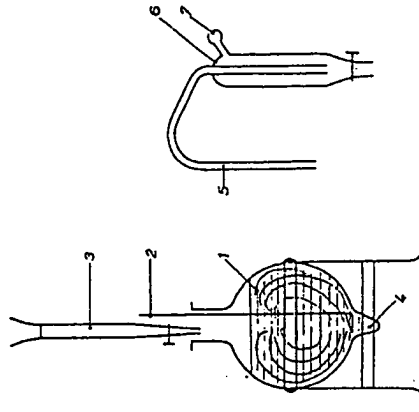


Fig. 5